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MAUFACTURING METHOD OF BAKE-HARDENABLE STEEL SHEET WITH LESS AGING
DEGRADATION
[Jikou rekka no sukunai yakitsuke koukasei kouban no seizou houhou]

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[Claim 1] A manufacturing method of a bake-hardenable steel sheet with a low aging degradation characterized in that a steel piece, having a composition of C: not greater than 0.01 wt%, Si: not greater than 0.10 wt%, Mn: not greater than 1.5 wt%, P: not greater than 0.20 wt%, S: not greater than 0.010 wt%, Al: 0.030 ~ 0.150 wt%, N: not greater than 0.0040 wt%, and the rest being Fe and inevitable impurities, is hot-rolled at a finish rolling temperature of 800 ~ 950°C and is taken up at 600°C or higher to form a hot-rolled sheet, which is acid-washed, cold-rolled and subjected to an annealing process under an atmosphere of a gas mixture of hydrogen in an amount of at least 3% with the rest being practically nitrogen and a dew point of at least -20°C at a temperature of the recrystallization temperature or higher for at least 10 seconds to carry out the decarburization-annealing with the amount of decarburization of at least 0.0005 wt%, then subjected to a secondary cold-rolling process at a rolling reduction ratio of 1 ~ 5%.

[Claim 2] The manufacturing method of the bake-hardenable steel sheet with a low aging degradation as described in Claim 1, wherein said steel composition further contains 1 element or 2 elements selected from Nb: 0.003 ~ 0.040 wt% and Ti: 0.003 ~ 0.040 wt% and Nb and Ti each satisfies the following formulas:

$$\{Nb \text{ (wt\%)} / 93\} / \{C \text{ (wt\%)} / 12\} \leq 0.8, \text{ and}$$

*Claim and paragraph numbers correspond to those in the foreign text..

$$\{Ti*(wt\%)/48\}/\{C(wt\%)/12\} \leq 0.8,$$

{wherein in the above formula, $Ti*(wt\%) = Ti(wt\%) - (48/32) \times S(wt\%) - (48/14) \times N(wt\%)$ }.

[Claim 3] The manufacturing method of the bake-hardenable steel sheet with a low aging degradation as described in Claim 1 or 2, wherein said steel composition further contains B: 0.0002 ~ 0.0020 wt%.

[Claim 4] The manufacturing method of the bake-hardenable steel sheet with a low aging degradation as described in any one of Claims 1, 2 and 3, wherein said steel composition further contains 1 element or at least 2 elements selected from Cu: 0.01 ~ 0.2 wt%, Ni: 0.01 ~ 0.2 wt%, Cr: 0.01 ~ 0.2 wt% and Mo: 0.01 ~ 0.2 wt%.

[Claim 5] The manufacturing method of the bake-hardenable steel sheet with a low aging degradation as described in any one of Claims 1, 2, 3, and 4, wherein in said hot-rolled steel sheet, at least 80% of the amount of N in the steel is precipitated as AlN.

[Detailed explanation of the invention]

[0001] [Technical area to which the invention belongs]

The present invention relates to a manufacturing method of a bake-hardenable steel sheet. In particular, the present invention relates to a manufacturing method of a steel sheet appropriate for use in the area in which dent resistance after forming is required, such as an automobile panel, and exhibiting less aging degradation and excellent bake hardenability.

[0002] [Prior arts]

A bake-hardenable steel sheet for press forming is normally soft during forming and ideally has a characteristic of being hardened by heat treatment (around 170°C x 20 minutes) during the baking process after subjecting to forming and coating processes to form a final product with sufficient strength. Several research studies have been carried out in the past years to develop a steel sheet exhibiting such characteristics. For example, in JP-A (Tokkai) Hei5-48283, a method of controlling the content of the dissolved C within the optimum range by specifying the composition of steel is described. Also in JP-A (Tokkai) Sho57-192225, as a similar technology, a method of controlling the amount of C in the dissolved state by adding Nb instead of Ti and by controlling the behavior of the dissolution and precipitation of Nb is described. In this method, the steel is annealed at a high temperature in the range of 850°C or higher to re-dissolve a portion of precipitated NbC, then quenched for prevention of re-precipitation to ensure the content of the dissolved C in an appropriate range.

[0003] [Problem to be solved by the invention]

However, even with these new technologies, it has been difficult to meet the recent level of customer demand for a bake-hardenable steel sheet. That is, the concrete characteristics which are required for the bake-hardenable steel sheet are excellent bake hardenability (at least 40 MPa), excellent r value, and a low room-temperature aging degradation characteristic. It has been difficult to achieve both good bake hardenability and the room-temperature aging degradation resistance

simultaneously using the current technologies. That is, when the dissolved C content is increased to ensure the high bake hardenability, the room-temperature aging degradation resistance becomes deteriorated and a risk of forming a stretcher strain during a press-forming becomes high, which damages the surface appearance. Currently, an industrial manufacturing method of achieving both characteristics simultaneously has not been developed.

[0004] As examples of the current technologies which suppress the stretcher strain while maintaining high bake hardenability, the following methods can be mentioned:

a) a method of carburization while an atmosphere is controlled during the annealing process (for example, Japanese Patent Publication Hei8-14019);

b) a method of continuous annealing of an ultra-low carbon steel under a 2-phase region (for example, Japanese Patent Publication Hei2-232316) and the like. However, both methods have problems in terms of uniformity in the material quality and stable operation. In the method a), since the furnace is maintained under a strong carburization atmosphere, the treatment of a material which is not subjected to the carburization in the same production line has been difficult. In the method b), it is necessary to use a special component system for the composition of the steel sheet.

[0005] Furthermore, according to the investigation of the present inventors, the current accelerated testing method employed in the current technologies to study the room-temperature aging degradation

characteristics, which has been established based on the empirical rule of the time-temperature equivalence and measured at around 100°C, does not simulate the actual aging degradation characteristic of the steel sheet. Also, it has been discovered that a better measurement method for the room temperature aging degradation that provides a better simulation characteristic is to employ the most severe condition which the steel sheet would experience under normal storage conditions, around 50°C (at which temperature the steel sheets would be stored when they pass through the equatorial line during the export transportation and the like). Therefore, the development of a bake-hardenable steel sheet which withstands the above-mentioned accelerated room temperature aging degradation testing which correctly reflect the actual use environment is desired.

[0006] The main purpose of the present invention is to solve the problems which the current technologies have. That is, the purpose of the present invention is to provide a method of manufacturing a steel sheet exhibiting a high bake hardenability so that a part, after subjecting to the press forming, coating and baking, would exhibit sufficient strength and aging degradation resistance (will not generate a stretcher strain during the press forming) without causing non-uniformity in quality nor operational instability. Also, the concrete purpose of the present invention is to provide a manufacturing technology of a steel sheet exhibiting a bake hardenability (BH) of at least 40 MPa, a yield point elongation of 0.2% or less after 3 months at 50°C and a r value (in-plane average) of at least

1.8 without causing disadvantages such as non-uniformity in quality nor unstable operation.

[0007] [Means to solve the problem]

The present inventors have done many experiments and research work pertaining to the steel components, roll conditions, heat treatment conditions and the like, to solve the above problems and have reached the following conclusions:

1) For the steel components, the ultra-low carbon steel which exhibits a high r value is appropriate. Also, it is an effective method to add a carbonitride-forming element selectively to ensure the amount of dissolved C from the standpoint of the quality stabilization of the material.

2) By aggressively applying the decarburization phenomenon, the phenomenon which has been tried to eliminate as much as possible in a conventional continuous annealing process, to the above ultra-low carbon steel, desired material characteristics can be obtained. That is, in the continuous annealing process, the decarburization reaction is promoted on the steel surface at a dew point of -20°C or higher to reduce the aging effect, while inside the steel, a sufficient concentration of the dissolved C is maintained to ensure the high bake hardenability. In the above method, it has become possible to obtain characteristics of the bake hardenability and the aging degradation resistance simultaneously.

[0008] The present invention has been established based on the above findings. The summary of the present invention will be described below.

1) A manufacturing method of a bake-hardenable steel sheet with a low aging degradation, characterized in that a steel piece, having a composition of C: not greater than 0.01 wt%, Si: not greater than 0.10 wt%, Mn: not greater than 1.5 wt%, P: not greater than 0.20 wt%, S: not greater than 0.010 wt%, Al: 0.03 ~ 0.150 wt%, N: not greater than 0.0040 wt%, and the rest being Fe and inevitable impurities, is hot-rolled at a finish rolling temperature of 800 ~ 950°C and is taken up at 600°C or higher to form a hot-rolled sheet, which is acid-washed, cold-rolled and subjected to an annealing process under an atmosphere of a gas mixture of hydrogen in an amount of at least 3% with the rest being practically nitrogen and a dew point of at least -20°C at a temperature of the recrystallization temperature or higher for at least 10 seconds to carry out the decarburization-annealing with the amount of decarburization of at least 0.0005 wt%, then subjected to a secondary cold-rolling process at a rolling reduction ratio of 1 ~ 5%.

[0009] 2) The manufacturing method of the bake-hardenable steel sheet with a low aging degradation as described in 1), wherein the steel composition further contains 1 element or 2 elements selected from Nb: 0.003 ~ 0.040 wt% and Ti: 0.003 ~ 0.040 wt% and Nb and Ti each satisfies the following formulas:

$$\{Nb \text{ (wt\%)} / 93\} / \{C \text{ (wt\%)} / 12\} \leq 0.8, \text{ and}$$

$$\{Ti * \text{(wt\%)} / 48\} / \{C \text{(wt\%)} / 12\} \leq 0.8,$$

{wherein in the above formula, $Ti^*(wt\%) = Ti(wt\%) - (48/32) \times S(wt\%) - (48/14) \times N(wt\%)$ }.

[0010] 3) The manufacturing method of a bake-hardenable steel sheet with a low aging degradation as described in 1) or 2), wherein the steel composition further contains B: 0.0002 ~ 0.0020 wt%.

[0011] 4) The manufacturing method of the bake-hardenable steel sheet with a low aging degradation as described in any one of 1), 2) and 3), wherein the steel composition further contains 1 element or at least 2 elements selected from Cu: 0.01 ~ 0.2 wt%, Ni: 0.01 ~ 0.2 wt%, Cr: 0.01 ~ 0.2 wt% and Mo: 0.01 ~ 0.2 wt%.

[0012] 5) The manufacturing method of the bake-hardenable steel sheet with a low aging degradation as described in any one of 1), 2), 3), and 4), wherein in the hot-rolled steel sheet, which is a mother steel sheet for the cold-rolled sheet, at least 80% of the amount of N in the steel is precipitated as AlN.

[0013] [Mode of the execution of the invention]

The reasons for setting the component composition, the manufacturing conditions and the like as shown above will be explained below.

(1) About steel component.

C: 0.01 wt% or less.

C is a harmful element in terms of formability. By reducing C, a stable and high r value and excellent ductility can be obtained. To obtain the above effects, it is necessary that the C content is 0.01 wt% or less. When

the r value is taken into consideration, the C content is preferably 0.004 wt% or less. Also, to obtain the effective bake hardenability, the C content is preferably at least 0.001 wt%.

[0014] Si: 0.10 wt% or less.

Since Si causes deteriorated surface treatability and corrosion resistance when added too much, the upper limit is 0.10 wt%. When the higher corrosion resistance is required, the Si content is preferably limited to 0.02 wt% or less.

[0015] Mn: 1.5 wt% or less.

Since Mn is an effective element to prevent cracking during hot working operation due to S, its content is adjusted appropriately corresponding to the S content. Also, Mn is an effective element for quality improvement since it has a grain refining effect. To obtain above effects, the Mn content is preferably at least 0.1 wt%. However, when its content is too much, the corrosion resistance and the flange formability become deteriorated although strengthening of the steel sheet can be achieved. Therefore, the upper limit of the Mn content is 1.5 wt%. In the application in which better formability is required, the Mn content is preferably 0.80 wt% or less.

[0016] P: 0.20 wt% or less

Although P is a useful element for strengthening a solid solution, excessive use of P causes hardening of the steel, resulting in the deteriorated flange formability or neck formability, in addition to a deteriorated corrosion resistance. Therefore, the upper limit of the P content is set as 0.20 wt%. When the formability and the corrosion resistance

need to be emphasized, the upper limit of the P content is preferably set at 0.01 wt% or less.

[0017] S: 0.010 wt% or less

S is present as an inclusion and causes deteriorated ductility and corrosion resistance. These effects become noticeable when the S content exceeds 0.010 wt%. Therefore, the upper limit of the S content was set at 0.010 wt%. When especially excellent formability is required, the S content is preferably controlled to 0.005 wt% or less.

[0018] Al: 0.030 ~ 0.150 wt%

Al is a necessary element to fix N stably and requires at least 0.03 wt%. However, an excess Al causes a deterioration in the surface properties, increased anisotropy in the rolling direction, a flange cracking due to the softened welded part and the like. Therefore, for the further stabilization of the material quality, Al is added in an amount of 0.040 ~ 0.080 wt%.

[0019] N: 0.0040 wt% or less

N is an element increasing an aging property and exhibits high solubility in ferrite. Therefore, a control of the amount of dissolution of this element is important. In the present invention, the intension is to achieve the bake hardenability solely by C, not relying on N. By the addition of Al, the amount of dissolution of N can be reduced. However, when the total amount of N exceeds 0.0040 wt%, a stable fixation of dissolved N becomes difficult. Therefore, the N content is set as 0.0040 wt% or less, or preferably 0.0020 wt% or less.

[0020] In addition to the above fundamental elements, following elements can be selectively added.

Nb: 0.003 ~ 0.04 wt% and $\{Nb \text{ (wt\%)} / 93\} / \{C \text{ (wt\%)} / 12\} \leq 0.8$

Nb has an effect of reducing dissolution of C and N by forming a carbonitride and has a noticeable effect of refining the grain size. These effects can be observed at an amount of at least 0.003 wt%. However, when the amount exceeds 0.040 wt%, the steel becomes hardened, causing trouble during the cold rolling process and increasing the risk of cracking during the continuous slab casting process. Therefore, the upper limit of the Nb

content is set at 0.04 wt%. However, when a high bake hardenability needs to be ensured, the upper limit is preferably 0.02 wt%. Also when the atomic ratio of Nb and C, that is, $\{Nb \text{ (wt\%)} / 93\} / \{C \text{ (wt\%)} / 12\}$, exceeds 0.8, it becomes difficult to achieve the desired high bake hardenability. Therefore, the above atomic ratio is set at 0.8 or less, or more preferably at 0.75 or less.

[0021] Ti: 0.003 ~ 0.040 wt% and $\{Ti^* \text{ (wt\%)} / 48\} / \{C \text{ (wt\%)} / 12\} \leq 0.8$. In the formula, $Ti^* \text{ (wt\%)} = Ti \text{ (wt\%)} - (48/32) \times S \text{ (wt\%)} - (48/14) \times N \text{ (wt\%)}.$

Similar to Nb, Ti has the effect of reducing the dissolved C and has the effect of refining the grain size. These effects can be observed at an amount of at least 0.003 wt%. However, when the amount exceeds 0.04 wt%, the bake hardenability becomes deteriorated. Therefore, the Ti content is set in the range of 0.003 ~ 0.04 wt%. To ensure the stable bake hardenability, the Ti content is preferably set in the range of 0.005 ~ 0.020 wt%. Also,

when the atomic ratio of Ti to C, that is, $\{Ti*(wt\%)/48\}/\{C(wt\%)/12\}$, [in the formula, $Ti*(wt\%) = Ti(wt\%) - (48/32) \times S(wt\%) - (48/14) \times N(wt\%)$], exceeds 0.8, it becomes difficult to obtain the desired bake hardenability. Therefore, the above atomic ratio is set at 0.8 or less, or preferably 0.75 or less.

[0022] B: 0.0002 ~ 0.0020 wt%

Although its mechanism has not been completely elucidated, B is an effective element in improving the room-temperature aging characteristic without hurting the bake hardenability of the steel sheet. Such effects can be observed at the addition amount of at least 0.0002 wt%. The amount exceeding 0.0020 wt% causes not only a saturation in the effect, but also an increase in the in-plane anisotropy of the mechanical characteristics of the steel sheet. Therefore, this element is added in an amount ranging from 0.0002 ~ 0.0020 wt%, or more preferably ranging from 0.0005 ~ 0.0010 wt% in terms of stabilization and uniformization of the mechanical properties.

[0023] Cu: 0.01 ~ 0.2 wt%, Ni: 0.01 ~ 0.2 wt%, Cr: 0.01 ~ 0.2 wt%, and Mo: 0.01 ~ 0.2 wt%

Cu, Ni, Cr and Mo exhibit almost similar material improvement effect. They can improve the strength of the steel without causing a large deterioration in ductility. Such an effect can be observed at the addition amount of at least 0.01 wt%. When the amount exceeds 0.2 wt%, a saturation in the effect can be observed and a risk of causing hardening of the hot-rolled

mother sheet increases, which may cause trouble during the cold rolling process. Since above effects are not wiped out by the addition of a combination of the above elements, they can be added alone or can be added as a mixture.

[0024] (2) Manufacturing condition

Hot rolling

The steel raw material before hot rolling process is subjected to a solution heat treatment at a temperature of the Ac_3 point or higher, or more concretely in the range of preferably $1,050 \sim 1,300^\circ\text{C}$. In the following hot rolling process, a finish rolling temperature is important to ensure the r value and the ductility of the steel sheet. To obtain a desired high r value and a high bake hardenability, it is necessary that the finish rolling temperature is set at 800°C or higher. However, when the finish rolling process is carried out at a temperature exceeding 950°C , a load to the hot roll increases and the structure becomes coarse. Therefore, the finish rolling temperature is set at $800 \sim 950^\circ\text{C}$, or preferably $840 \sim 920^\circ\text{C}$.

[0025] Take-up temperature

The take-up temperature influences the stable fixation of N by Al. By setting the take-up temperature at 600°C or higher, preferably 650°C or higher, a precipitation-fixation of N by Al can be achieved over an entire length of hot-rolled coil. Although there is no upper limit about the take-up temperature, it is preferably 780°C or lower taking the control of worsening of descalability into consideration.

[0026] In the hot rolled sheet, at least 80% of N in the steel is precipitated as AlN.

The hot-rolled sheet is acid-washed, cold-rolled and subjected to a continuous annealing. During this annealing, a portion of dissolved N is precipitated as AlN. However, since the treatment time is short, it is difficult to precipitate all of dissolved N. When N in a dissolved state is present after annealing, the aging degradation at a room temperature, especially a recovery of the yield point elongation, becomes noticeable. For that reason, it is preferable that at least 80%, or more preferably at least 85%, of N in the steel is precipitated at the stage of the hot rolled sheet. The N in the precipitation state defined above means the N content (N as AlN) which is calculated from the equivalent relation after analyzing AlN by a conventional electrolytic extraction analysis method. To maintain the amount of N which is subjected to precipitation-fixation within the above-described range, the control of the above-mentioned take-up temperature after the hot rolling is extremely important. Besides, retention of the wound coil under heating for at least 1 hour or slow cooling of the wound coil is also a powerful method.

[0027] Continuous annealing

The continuous annealing process is one of the most important subjects in the present invention. The continuous annealing is carried out in an atmosphere of a gas composition containing hydrogen in an amount of at least 3% with the rest being nitrogen and a dew point of at least -20°C at a recrystallization temperature or higher for at least 10 seconds. During

the annealing process, the steel is subjected to a decarburization (carbon elimination) in an amount of at least 0.0005 wt%. At the final decarburization amount of at least 0.0005 wt%, achieving both sufficient bake hardenability and excellent room temperature aging degradation resistance simultaneously, which are the objectives of the present invention, becomes possible. Although the detailed mechanism of decarburization has not been completely elucidated, it is postulated as follows. In the decarburization reaction, the C in the steel is removed from the surface of the steel in the form of CO (or may be CH₃ or CO₂) by the solid-gas reaction taking place at the surface. Therefore under a short non-equilibrium condition, a large concentration gradient of C is generated from the surface toward the inside of the steel. Although it is difficult to analyze the actual concentration distribution along the steel thickness, when the calculation is done assuming that the reaction rate is controlled by diffusion of C, the C concentration curve as shown in Figure 1 can be obtained. It can be confirmed that this analysis is reasonable to some extent from the fact that the integrated C content toward the thickness direction in Figure 1 closely matches the analytical result obtained by measuring the C contents of before and after annealing. Such a concentration gradient can be maintained even at room temperature when the steel is quenched (at least 10°C/sec) after soaking such as a continuous annealing.

[0028] When the steel sheet having the concentration gradient of C in the sheet thickness direction as shown above is subjected to a secondary rolling under the reduction ratio of 1 ~ 5%, a mobile dislocation is

introduced into the surface in which the content of C is extremely low. That is, a locking of the mobile dislocation introduced at the surface by C can be easily avoided, which leads to the manifestation of the excellent room temperature aging resistance. At the stage of using the product, it is subjected to a plastic work strain of at least around 5% before aging treatment at around 170C° for 20 minutes. In this case, deformation takes place over the entire sheet thickness direction and many new mobile dislocations are introduced. During the next aging treatment step, sufficient amounts of dissolved C remained inside the steel lock those large amounts of dislocations in position, which make it possible to provide a desired high bake hardenability characteristic.

[0029] As mentioned above, to cause the effective decarburization reaction, it is necessary that the steel sheet is to be subjected to the continuous annealing in which a rapid heating and a cooling are possible and that the annealing is carried out under the atmosphere containing hydrogen in an amount of at least 3% with the rest being practically nitrogen. Also, it is necessary that annealing is to be carried out at a dew point of -20°C or higher or preferably -10°C or higher. Also, the annealing temperature should be the recrystallization temperature or higher, with the annealing time of at least about 10 seconds, or preferably at least 20 seconds. Although there is no upper limit for the annealing time, it is preferably less than 40 seconds taking the efficiency of the production process into consideration. Also, although there is no upper limit for the hydrogen concentration, it is preferably 10% or less, taking the cost of

the environment gas and the stability of the operation into consideration. The amount of decarburization can be obtained by measuring the C content in the steel before and after the annealing using a method of the penetration analysis in the sheet thickness direction. When the difference in the C content is 0.0005 wt% or higher, the steel sheet with desired room temperature aging resistance characteristic and a sufficiently high bake hardenability can be obtained. Ideally, the C concentration profile in the depth direction should be taken into consideration. However, in the steel composition and the manufacturing conditions of the present invention, the penetration analysis method in the sheet thickness direction can be appropriately used as a substitute.

[0030] Secondary cold rolling

The secondary cold rolling is normally carried out under the low reduction ratio of around 0.8%. However in the present invention, it is necessary to carry out the secondary cold rolling under the higher reduction ratio to impart sufficient room temperature aging resistance. That is, by applying a reduction ratio of at least 1%, the yield point elongation due to aging after 50°C - 3 month can be suppressed to 0.2% or less. However, when the secondary cold rolling is carried out under a reduction ratio exceeding 5%, the steel exhibits deteriorated ductility, especially deteriorated uniform elongation, which will increase the risk of cracking during press forming. Therefore, the reduction ratio during the secondary cold rolling is set at 1 ~ 5%. Furthermore, when further improvement in

the room temperature aging resistance characteristic is required, the reduction ratio is preferably set at 2 ~ 3%.

[0031] The desired material characteristics of the present invention are: the r value (in-plane average) of at least 1.8; the bake hardenability (BH) of at least 40 MPa; and the yield point elongation after 50°C - 3 month of 0.2% or less. The bake hardenability guarantees the strength characteristic of the formed product during usage. Although its optimum value varies depending on the thickness of the steel sheet and the strength level, for a part made of the steel sheet of the present invention having an excellent formability, normally the bake hardenability of 40 MPa is sufficient for practical use. Concerning the room temperature aging characteristic, the steel sheet which withstands the aging of 50° - 3 month normally can be practically used although varying depending on the final part product. When the yield point elongation that is recovered after the above aging condition is 0.2% or less, the steel sheet does not exhibit the appearance defect due to the generation of stretcher strain during the press forming.

[0032] Example 1

The present invention will be explained using Examples. A steel having the component composition as shown in Table 1 was melted in a converter to form a steel slab. This steel slab was subjected to a hot rolling, a continuous annealing, and a secondary cold rolling under the conditions as shown in Table 2 to form a cold rolled steel sheet with a final sheet

thickness of 0.7 mm. From the obtained steel sheet, a JIS #5 testing sample was taken from a position at 1/4 the width of the steel sheet in the width direction for testing of conventional mechanical characteristics and the bake hardenability. For the room temperature aging testing, a similarly taken sample was placed in a constant temperature bath at 50°C for 3 months. The results are shown in Table 3. The bake hardenability (BH value) was obtained as follows. That is, the sample was subjected to a strain of 2%. After removal of the load, the sample was aged at 170°C for 20 minutes. Then the sample was subjected to the elongation again. The difference between the deformation stress before aging and the yield stress after aging was taken as the BH value. Also, the r value was obtained from the following formula as the average r value.

$$r = (r_0 + r_{90} + 2r_{45})/4,$$

wherein:

r_0 = the r value in the rolling direction

r_{90} = the r value in the direction 90 degree to the rolling direction

r_{45} = the r value in the direction 45 degree to the rolling direction

[0033] [Table 1]

1	鋼 No	2 化 学 组 成 (wt%)								3	備 考	4
		C	Si	Mn	P	S	Al	N	その他			
	1	0.0030	0.01	0.10	0.010	0.004	0.040	0.0015	Na/0.008		適合例	5
	2	0.0022	0.01	0.30	0.005	0.005	0.350	0.0018			適合例	
	3	0.0070	0.01	0.25	0.006	0.001	0.530	0.0025			適合例	
	4	0.0124	0.01	0.15	0.015	0.007	0.028	0.0020	71/0.006		適合例	
	5	0.0165	0.01	0.10	0.007	0.005	0.120	0.0022	Na/0.02		適合例	
	6	0.0012	0.01	0.45	0.006	0.015	0.581	0.0028	Na/0.006, P/0.0005		適合例	6
	7	0.0013	0.01	0.25	0.006	0.009	0.060	0.0011	Cu/0.05, Ni/0.05, Cr/0.05		適合例	
	8	0.0025	0.01	0.50	0.004	0.010	0.050	0.0012	Na/0.008, 71/0.005		適合例	
	9	0.0350	0.01	0.15	0.000	0.002	0.040	0.0015			比較例	

Key:

1. Steel composition
2. Chemical composition (wt%)
3. Others
4. Remark
5. Current Example
6. Comparative Example

[0034] [Table 2]

Slab heating temperature (°C)	Hot rolling		Take-up temperature (°C)	Cold rolling	
	Finish temperature (°C)	Final thickness (mm)		Thickness (mm)	Reduction ratio (%)
1150	880	2.6	700	0.73	72

Continuous annealing				Secondary cold rolling reduction ratio (%)
Temperature (°C)	Gas composition	Dew point (°C)	Time (sec)	
840	3% H ₂ , the rest N ₂	-10	30	2

[0035] [Table 3]

1	2	3	4	5	6	7	8	9	10
No.	N in the hot rolled sheet as AlN (%)	The amount of C after annealing (%)	The amount of decarburization (wt%)	The r value	Elongation (%)	TS (MPa)	BH (MPa)	Yield point elongation after room temperature aging (%)	Remark
1	95	0.0000	0.0021	2.1	49	319	45	0	発明例
2	90	0.0011	0.0011	2.0	48	315	47	0	発明例
3	95	0.0035	0.0035	1.8	45	338	51	0	発明例
4	85	0.0040	0.0034	1.6	45	343	50	0	発明例
5	85	0.0050	0.0025	1.8	45	350	52	0	発明例
6	95	0.0005	0.0005	2.0	49	309	41	0	発明例
7	95	0.0004	0.0009	1.9	46	350	53	0	発明例
8	90	0.0015	0.0010	1.9	47	330	48	0	発明例
9	82	0.0020	0.0030	1.1	43	352	50	7.0	比較例

Key:

1. Steel number
2. N in the hot rolled sheet as AlN (%)
3. The amount of C after annealing (%)
4. The amount of decarburization (wt%)
5. The r value
6. Elongation (%)
7. Yield point elongation after room temperature aging (%)
8. Remark
9. Examples of the present invention
10. Comparative Example

[0036] As shown in Table 1 ~ 3, the steel sheets prepared by the method of the present invention exhibited a high r value, high elongation (El) and a bake hardenability of at least 40 MPa, while maintaining excellent resistance to yield point elongation after severe aging, which suppresses the formation of an unacceptable appearance caused by generation of so-called stretcher strain. In the actual press forming, expected increase in the part strength due to excellent BH property and the suppression of the generation of stretcher strain were able to be achieved. Along with

the above experiments, similar experiments were carried out at the actual continuous molten zinc-plated steel sheet manufacturing line according to the annealing conditions which were within the range specified by the present invention. Similar to the above cold rolled steel sheets, the manufactured sheet exhibited excellent formability (high r value and high El) and a high BH property and did not exhibit degradation due to the room temperature aging. Therefore, it was confirmed that the present invention can be applied to manufacturing of not only a cold rolled steel sheet, but also to manufacturing of a molten zinc-plated steel sheet (and alloyed molten zinc-plated steel sheet). As might be expected, after manufacturing the cold rolled steel sheet of the present invention, it can be electroplated with zinc alloy or the like, without any trouble.

[0037] Example 2

Using the steel No. 1 having the chemical composition as shown in Table 1, the cold rolled steel sheets were manufactured according to the manufacturing conditions as shown in Table 4 and were electroplated in a continuous electroplating line to form Zn-Ni alloy-plated steel sheets. After that, the obtained steel sheets were coated with a resin and baked. Similar to Example 1, mechanical properties, a BH property and a room temperature aging degradation characteristic of the obtained products were investigated. The results are shown in Table 5. The resin-coated composite plated steel sheets manufactured by the present invention exhibited a high r value and a high elongation and a bake hardenability of at least 40 MPa, while maintaining excellent resistance to yield point elongation after

above-described severe aging conditions. Therefore, the steel sheets of the present invention do not exhibit any unacceptable appearances caused by the generation of so-called stretcher strain. Also, in the actual press forming, expected increase in the part strength due to excellent BH property and the suppression of the generation of stretcher strain were able to be achieved.

[0038] [Table 4]

No	1	2	3	4	5	6				11	12	13
	スラブ 加熱 温度 (℃)	熱延 仕上げ 温度 (℃)	熱延 温度 (℃)	N 中 量 as AlN (%)	圧下率 (%)	7	8	9	10	脱炭素 率 (%)	冷延 圧下率 (%)	備考
1	1150	880	880	90	75	850	50H ₂ - 50N ₂	-10	25	21	2	発明例
2	1160	900	710	95	75	880	40H ₂ - 60N ₂	-15	30	18	3	発明例
3	1160	910	650	85	80	840	60H ₂ - 40N ₂	-5	20	22	3	発明例
4	1190	850	700	90	73	840	50H ₂ - 50N ₂	0	15	25	2	発明例
5	1120	850	710	90	73	840	50H ₂ - 50N ₂	-10	20	22	1.5	発明例
6	1250	800	680	85	78	830	50H ₂ - 50N ₂	-15	35	20	2	発明例
7	1230	800	680	85	78	830	50H ₂ - 50N ₂	-15	20	20	2	発明例
8	1200	800	690	80	75	820	50H ₂ - 50N ₂	-10	15	23	2	発明例
9	1200	870	730	96	75	840	50H ₂ - 50N ₂	-10	20	22	1.5	発明例
10	1200	900	540	70	75	820	50H ₂ - 50N ₂	-10	20	20	1.5	比較例
11	1280	820	710	80	75	840	N ₂ - 100%	-10	20	1	1.5	比較例
12	1280	890	700	88	75	840	50H ₂ - 50N ₂	-10	20	22	1	比較例

Key for Table 4:

1. Slab heating temperature (°C)
2. Finish hot-rolling temperature (°C)
3. Take-up temperature (°C)
4. N in the hot rolled sheet as AlN (%)
5. Cold rolling reduction ratio (%)
6. Continuous annealing
7. Temperature (°C)
8. Gas composition
9. Dew point (°C)
10. Time (second)

11. The amount of decarburization(wt%)
12. Secondary cold rolling reduction ratio (%)
13. Remark
14. Example of the present invention
15. Comparative Example

[0039] [Table 5]

No	1 r 値	2 伸 長 (%)	TS (MPa)	BH (MPa)	3 室 温 下 の 降伏 点 の 伸 長 (%)	4 備 考
1	2.02	48	315	45	0	発明例
2	2.14	49	310	42	0	発明例
3	1.95	47	320	43	0	発明例
4	2.05	49	315	41	0	発明例
5	1.98	48	325	43	0	発明例
6	2.10	49	312	44	0	発明例
7	1.85	47	350	45	0	発明例
8	1.88	47	331	51	0	発明例
9	1.92	46	325	44	0	発明例
10	1.40	46	320	45	0.5	比較例
11	1.70	45	325	45	1.5	比較例
12	1.38	33	280	20	0	比較例

Key:

1. The r value
2. Elongation (%)
3. Yield point elongation after room temperature aging (%)
4. Remark
5. Example of the present invention
6. Comparative Example

[0040] [Effect of the invention]

As explained above, according to the present invention, the steel raw material having specified components in amounts within the specified range is subjected to a hot rolling, cold rolling and continuous annealing

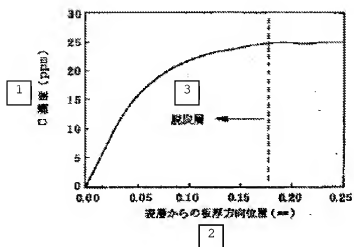
process. During the annealing process, the steel sheet is subjected to decarburization to aggressively form a C concentration gradient in the sheet thickness direction and is subjected to a temper rolling at a relatively high rolling reduction ratio. As a result, the obtained steel sheet can have properties of both sufficient coating bake hardenability and an excellent aging degradation resistance characteristic simultaneously, which has been difficult to achieve according to the conventional technologies. Therefore, the steel sheet of the present invention is soft during the press forming and assembly. When it is to be used as the product, it exhibits excellent strength due to bake hardening. Therefore, a down-gauging of the steel sheet in manufacture of a part having the same strength has become possible. As might be expected, the steel sheet of the present invention can be used as an original sheet for variety of plated sheets.

[Brief explanation of the figure]

[Figure 1]

Figure 1 shows the C concentration distribution in the sheet thickness direction obtained by the calculation.

Figure 1



Key:

1. The C concentration (ppm)
2. The position from the surface layer to sheet thickness direction (mm)
3. The decarburized layer

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(54) PRODUCTION OF STEEL SHEET HIGH IN BAKING HARDENABILITY
AND SMALL IN AGING DETERIORATION

(57)Abstract:

PROBLEM TO BE SOLVED: To production a steel sheet high in baking hardenability and free from the generation of aging deterioration without causing disadvantages in the points of the uniformity of the material and the stability of the operation.
SOLUTION: A slab having a compsn. contg., by weight, $\leq 0.01\%$ C, $\leq 0.10\%$ Si, $\leq 1.5\%$ Mn, $\leq 0.20\%$ P, $\leq 0.010\%$ S, 0.030 to 0.150% Al, $\leq 0.0040\%$ N, and the balance Fe with inevitable impurities is subjected to hot rolling so as to regulate the finish rolling temp. to 800 to 950°C and is coiled at $\geq 600^\circ\text{C}$, this hot rolled sheet is subjected to pickling and cold rolling, is thereafter subjected to decarburizing annealing by the quantity to be decarburized of $\geq 0.0005\text{wt.}\%$ by annealing treatment of holding to the recrystallization temp. or above for $\geq 10\text{sec}$ in an atmosphere in which the gaseous compsn. is composed of $\geq 3\%$ hydrogen, and the balance substantial nitrogen, and the dew point is regulated to $\geq -20^\circ\text{C}$ and is subjected to secondary cold rolling at a draft of 1 to 5%.

[Claim 1]C: Less than 0.01wt%, less than Si:0.10wt%, and less than Mn:1.5 wt%. P: Less than 0.20wt%, less than S:0.010 wt%, aluminum:0.030 - 0.150 wt%, Contain less than N:0.0040wt% and the remainder slab which becomes the presentation of Fe and inevitable impurities, Hot-roll by the finishing rolling temperature 800 - 950 **, and it rolls round above 600 **, After performing pickling and cold rolling to this hot-rolling board, not less than 3% of hydrogen and the remainder consist of nitrogen substantially, and gas composition in atmosphere whose dew point is more than -20 **, A manufacturing method of few baking hardenability steel plates of age deterioration carrying out decarburization annealing beyond amount of decarbonization 0.0005wt% to temperature more than recrystallizing temperature, and carrying out secondary cold

rolling of 1 to 5% of rolling reduction to it by an annealing process held 10 seconds or more.

[Claim 2] In claim 1, steel composition contains further one sort chosen from Nb:0.003 - 0.040 wt% and Ti:0.003 - 0.040 wt%, or two sorts, and this Nb and Ti are following formulas, respectively;
 $\{C (wt\%)/12\} \{Nb(wt\%)/93\} / 48 / \{C (wt\%)/12\} \leq 0.8$, however $Ti^*(wt\%) = Ti(wt\%) - (48/32) \times S(wt\%) - (48/14) \times N (wt\%)$ [≤ 0.8 and $\{Ti^*(wt\%)/48\}$]
A manufacturing method of few baking hardenability steel plates of age deterioration becoming the presentation with which ***** is filled.

[Claim 3] A manufacturing method of few baking hardenability steel plates of age deterioration, wherein steel composition turns into a presentation containing B:0.0002 - 0.0020wt% further in claim 1 or 2.

[Claim 4] In any 1 paragraph of claims 1-3, steel composition further Cu:0.01 - 0.2 wt%, nickel: A manufacturing method of few baking hardenability steel plates of age deterioration becoming the presentation containing any one sort chosen from Cr:0.01 - 0.2 wt% and Mo:0.01 - 0.2 wt%, or two sorts or more 0.01 - 0.2 wt%.

[Claim 5] A manufacturing method of few baking hardenability steel plates of age deterioration given in any 1 paragraph of claims 1-4 depositing not less than 80% of the amount of N in steel as AlN in a hot-rolling board.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacturing method of a baking hardenability steel plate.

Like especially the panels of a car, the dent-proof nature after processing uses for the required purpose for spending, and it is related with the suitable manufacturing method of the steel plate which there is little age deterioration, it moreover prints and has hardenability.

[0002]

[Description of the Prior Art] As for the baking hardenability steel plate for press working of sheet metal, what can manufacture the processed products which are elasticity in the time of shaping, generally have the characteristic made hard in the baking process after fabricating and painting by heating (in general 170 °C x 20 minutes) processing, and were eventually provided with sufficient intensity is ideal. From the former, some researches for giving such the characteristic have been done. For example, the method which is going to control the amount of dissolution C in steel in the proper range is indicated by JP,5-48283,B by mainly specifying a steel composition. the method of controlling the amount of C of a dissolution state is indicated by JP,57-192225,A by adding Nb instead of Ti and controlling the dissolution of Nb, and a deposit action as similar art. By carrying out elevated-temperature annealing above 850 °C, making a part of NbC of a

separation state re-dissolve, and quenching from that state, this method tends to prevent a re-deposit and tends to secure the amount of dissolution C of an appropriate range.

[0003]

[Problem(s) to be Solved by the Invention]However, the region which fills the latest request level in a baking hardenability steel plate also by such conventional technologies is not arrived at. That is, the concrete characteristics demanded were high baking hardenability (40 or more MPa), a good r value, and the low room temperature age deterioration characteristic, and were difficult to reconcile baking hardenability and the room temperature age deterioration characteristic especially in the above-mentioned conventional technology. That is, when it is going to secure the big amount of baking hardening and the amount of dissolution C was made to increase, the room temperature prescription characteristic deteriorates, there is a danger of generating a stretcher strain at the time of press forming, and becoming an appearance defect, and the manufacturing method with which it can be industrially satisfied of both the characteristics did not exist.

[0004]How to control atmosphere by a annealing process and carburize as conventional technology which prints controlling a stretcher strain and makes hardenability profitably like (for example, JP,8-14019,B)

b) How to carry out continuous annealing of the extremely low carbon steel in a two-phase region (for example, JP,2-232316,A)

Although there was ****, all had a problem in respect of the homogeneity of construction material, and the stability of operation. In the above-mentioned a, since the furnace atmosphere was made into strong carburization atmosphere, when processing the material which does not perform carburization in an identical line, the problem had especially been produced. In the above-mentioned b, the problem of being indispensable has also made the presentation of a steel plate into a special component system.

[0005]In order to measure the room temperature age deterioration characteristic according to artificers' investigation examination, The fact carried out at the temperature of about 100 ** based on the rule of thumb about the equivalence of temperature and time adopted also in the above-mentioned conventional technology that actual age deterioration could not be simulated in the conventional accelerated test became clear. And as a measuring method of the room temperature age deterioration characteristic with more sufficient simulation nature, the good thing was also understood that it makes prescription temperature into an about 50 ** elevated temperature (it becomes storage at a temperature of this level when performing export etc., and passing through the equator) in consideration of the severest conditions that may be attained in the usual state of preservation. An appearance of the baking hardenability steel plate which can also bear the right valuation method of the room temperature age deterioration characteristic based on the actual operating environment from such a thing was desired.

[0006]Then, while the main purpose of this invention has big baking hardenability so that the parts which carried out after [press forming] paint baking can secure sufficient intensity in view of the problem which the above-mentioned conventional technology was holding, It is in providing the art of manufacturing the steel plate which does not

produce age deterioration (stretcher-strain generating at the time of press forming) without causing disadvantage in respect of the homogeneity of construction material, or the stability of operation. The amount of baking hardening (BH) the concrete purpose of this invention 40 or more MPa, The breakdown point elongation after the prescription for 50 ** to three months. 0.2% or less and an r value (field Hitoshi Uchihira) are 1.8. It is in providing the art of manufacturing the steel plate which has the above construction material characteristic without causing disadvantage in respect of the homogeneity of construction material, or the stability of operation.

[0007]

[Means for Solving the Problem]Artificers acquired knowledge shown below, as a result of repeating an experiment and research wholeheartedly about a steel composition, rolling, a heat treatment condition, etc., in order to solve the above-mentioned problem.

1) Extremely low carbon steel in which a high r value is obtained easily is [steel composition] suitable. It is also effective from a viewpoint of stabilization of construction material to add a carbon nitride formation element selectively and to secure the amount of C of a dissolution state.

2) In the conventional continuous annealing process, the target construction material characteristic is obtained by using positively for the above-mentioned extremely low carbon steel a decarbonization phenomenon in an annealing furnace for which it was striving to control as much as possible. That is, it becomes possible by making the dew point high with more than -20 **, printing inside a steel plate and making sufficient dissolution C to secure hardenability remain by a continuous annealing process, while producing decarbonization in a steel sheet surface and reducing prescription nature to reconcile baking hardenability and age deterioration-proof nature.

[0008]This invention is constituted based on the above knowledge, and the place made into the gist is as follows.

1) Less than C:0.01wt%, less than Si:0.10wt%, and less than Mn:1.5 wt%. P: Less than 0.20wt%, less than S:0.010 wt%, aluminum:0.030 - 0.150 wt%, Contain less than N:0.0040wt% and the remainder slab which becomes the presentation of Fe and inevitable impurities, Hot-roll by the finishing rolling temperature 800 - 950 **, and it rolls round above 600 **, After performing pickling and cold rolling to this hot-rolling board, not less than 3% of hydrogen and the remainder consist of nitrogen substantially, and gas composition in atmosphere whose dew point is more than -20 **, A manufacturing method of few baking hardenability steel plates of age deterioration carrying out decarburization annealing beyond amount of decarbonization 0.0005wt% to temperature more than recrystallizing temperature, and carrying out secondary cold rolling of 1 to 5% of rolling reduction to it by an annealing process held 10 seconds or more.

[0009]2) In the above 1, steel composition contains further one sort chosen from Nb:0.003 - 0.040 wt% and Ti:0.003 - 0.040 wt%, or two sorts, and this Nb and Ti are following formulas, respectively;

$\{C \text{ (wt\%)} / 12\} \{Nb \text{ (wt\%)} / 93\} / 48 / \{C \text{ (wt\%)} / 12\} \leq 0.8$, however $Ti^* \text{ (wt\%)} = Ti \text{ (wt\%)} - (48/32) \times S \text{ (wt\%)} - (48/14) \times N \text{ (wt\%)} [\leq 0.8 \text{ and } \{Ti^* \text{ (wt\%)} / 48\}]$

A manufacturing method of few baking hardenability steel plates of age deterioration becoming the presentation with which ***** is filled.

[0010]3) A manufacturing method of few baking hardenability steel plates of age deterioration, wherein steel composition turns into a presentation containing B:0.0002 - 0.0020wt% further in the above 1 or 2.

[0011]In any one of the above 1-3, steel composition further 4) Cu:0.01 - 0.2 wt%, nickel: A manufacturing method of few baking hardenability steel plates of age deterioration becoming the presentation containing any one sort chosen from Mo:0.01 - 0.2 wt%, or two sorts or more 0.01 - 0.2 wt%Cr:0.01 - 0.2 wt%.

[0012]5) A manufacturing method of few baking hardenability steel plates of age deterioration of any one statement of the above 1-4 depositing not less than 80% of the amount of N in steel as AlN in a hot-rolling board which is a cold-rolled negative.

[0013]

[Embodiment of the Invention]Next, the reason which limited component composition, manufacturing conditions, etc. as the above-mentioned gist composition is explained. (1) Less than C:0.01wt%C is a harmful element from processability about a steel composition, and the stable high r value and good ductility can be obtained by reduction of C. In order to acquire such an effect, when it is necessary to make the amount of C less than 0.01wt% and the field of an r value is taken into consideration, decreasing to less than 0.004 wt% is desirable. moreover -- in order to acquire effective baking hardenability -- in general -- more than 0.001 wt% -- it is preferred to make it contain.

[0014]Si: If it adds [less than 0.10wt%Si] so much, since degradation of surface treatment nature, corrosion-resistant degradation, etc. will be caused, it makes the maximum 0.10wt%. When the especially outstanding corrosion resistance is required, restricting to less than 0.02wt% is preferred.

[0015]Mn: When less than 1.5 wt%Mn prevents hot tearing resulting from S, it is an effective element, and it is good to add according to the amount of S to contain. Mn carries out minuteness making of the crystal grain, and is an element effective in improvement in construction material. in order to demonstrate these effects -- more than 0.1 wt% -- adding is desirable. On the other hand, since corrosion resistance will fall and flange processability will deteriorate although high intensity-ization of a steel plate can be attained if Mn is added so much, a maximum is made into 1.5 wt%. For the use as which a better moldability is required, less than 0.80wt% is desirable.

[0016]P: When less than 0.20wt%P attained high intensity-ization by solid-solution-strengthening operation, it was a useful element, but when contained so much, while making steel make it hard and degrading flange processability and neck processability, in order to reduce corrosion resistance, it made the maximum 0.20wt%. When thinking processability and corrosion resistance as important, it is preferred to hold down to less

than 0.01wt%.

[0017]S: Less than 0.010 wt%S is an element which exists as inclusion in steel, decreases ductility, and brings about further corrosion-resistant degradation. Since these influences will appear notably if S content exceeds 0.010 wt%, they are restricted to less than 0.010 wt%. It is desirable to control especially for the use as which good processability is required at less than 0.005 wt%.

[0018]Although aluminum:0.030 -0.150 wt%aluminum is an element required since it is stabilized and N is fixed and addition beyond 0.030 wt% is required for it, Since it will lead to the phenomenon of generating of the flange crack by degradation of a surface disposition, increase of the anisotropy of a rolling direction, and elasticity-izing of a weld zone if contained so much, the maximum is made into 0.150 wt%. In order [of construction material / further] to be stable, it is desirable to add in 0.040 - 0.080 wt% of the range.

[0019]N: Less than 0.0040wt%N is an element to which prescription nature is made to increase, and is an element in which the degree of dissolution in the inside of a ferrite is also large, and control of the amount of dissolution is important. In this invention, the baking hardening characteristic was not depended on N, but it aims at obtaining only by C. Although the amount of dissolution of N is reduced and being got by the above-mentioned addition aluminum, it becomes difficult to be stabilized if the total amount of N in steel exceeds 0.0040wt%, and to fix the dissolution N. therefore, the amount of N -- less than 0.0040wt% -- less than 0.0020wt% is used preferably.

[0020]The element stated to the next other than the above basic element can be added selectively.

Nb: By forming carbon nitride, 0.003 - 0.040 wt%, and $\{Nb(wt\%) / 93\} / \{C (wt\%) / 12\} \leq 0.8$ Nb are effective in reducing the dissolution C and N, and its minuteness making effect of a crystal grain is also remarkable. Although these effects are demonstrated by addition beyond 0.003 wt%, if it adds exceeding 0.040 wt%, steel will become hard and the danger of it not only causing trouble, but generating a crack at a slab casting process at a cold rolling process will increase. Therefore, although the maximum of the addition of Nb is made into 0.040 wt%, it is desirable to consider it as 0.02wt%, for it is stabilized and securing the amount of baking hardening. If the atomic ratio of Nb and C, i.e., $\{Nb(wt\%) / 93\} / \{C (wt\%) / 12\}$ exceeds 0.8, it will become difficult to acquire the baking hardenability of sufficient target quantity. For this reason, it is said atomic ratio 0.8 0.75 or less are used preferably hereafter.

[0021]Ti:0.003 - 0.040 wt%, and $\{Ti^*(wt\%) / 48\} / \{C (wt\%) / 12\} \leq 0.8$ however $Ti^*(wt\%) = Ti(wt\%) - (48/32) \times S(wt\%) - (48/14) \times N (wt\%)$

Ti is also an element effective in reducing the amount of dissolution C like Nb, and the minuteness making of an organization. Although such an effect is demonstrated by addition beyond 0.003 wt%, it will print, if it adds exceeding 0.04wt%, and the amount of hardening falls. Therefore, as for the addition of Ti, it is desirable to consider [which is made into 0.003 - 0.040 wt%] it as 0.005 - 0.020 wt% of the range in addition, in order

to be stabilized and to secure the amount of baking hardening. The atomic ratio of Ti and C, i.e., $\{Ti(wt\%)/48\} / \{C(wt\%)/12\} \leq 0.8$. However, if $Ti(wt\%) = Ti(wt\%)-(48/32) \times S(wt\%)-(48/14) \times N(wt\%)$ ** exceeds 0.8, it will become difficult to acquire the baking hardenability of sufficient target quantity. For this reason, it is said atomic ratio 0.8 0.75 or less are used preferably hereafter.

[0022]B: 0.0002-0.0020wt%B is an alloying element effective in improving the room temperature-proof prescription characteristic, without reducing the baking hardenability of a steel plate, although a detailed mechanism is not necessarily clear. Although such an effect is demonstrated by addition beyond 0.0002wt%, since this effect is not only saturated, but the plane anisotropy of the mechanical property of a steel plate will increase if it adds exceeding 0.0020wt%, it is added in 0.0002 - 0.0020wt% of the range. It is preferred to add in 0.0005 - 0.0010wt% of the range from the point of stabilization of mechanical properties and equalization.

[0023]Cr:0.01 - 0.2 wt% and Mo;0.01-0.2 wt%Cu, nickel, Cr, and Mo nickel:0.01 - 0.2 wt% Cu:0.01 - 0.2 wt%, The intensity of a steel plate can be made to increase, without having an almost similar construction material improvement effect, and causing ductile big degradation. Although such an effect is demonstrated from addition beyond 0.01wt%, even if it adds exceeding 0.2 wt%, the danger that in addition to an effect being saturated a hot-rolling motherboard will become hard and will generate the fault in a cold rolling process increases. Since the above-mentioned effect is not offset even if it carries out compound addition of these elements, either of independent addition and compound addition is obtained.

[0024](2) About manufacturing conditions, perfect solution-ization should just be made and heating of the steel stock before - hot-rolling hot-rolling should just be heated beyond A_c3 point. Specifically, 1050-1300 ** is suitable. In hot-rolling following the above-mentioned heating, finishing rolling temperature is important from the r value of a steel plate, and a viewpoint of ductile reservation. And in order to print with a high target r value and to obtain the hardening characteristic, it is finishing rolling temperature. It is required to consider it as not less than 800 **. However, when it rolls by finishing exceeding 950 **, the load of hot-rolling RORUHE increases, and also big and rough-ization of an organization also becomes remarkable. therefore, finishing hot-rolling temperature 800-950 ** -- it is preferably considered as the temperature requirement of 840 - 920 **.

[0025]- Rolling-up temperature rolling-up temperature affects the immobilization where N by aluminum was stabilized. rolling-up temperature -- not less than 600 ** -- desirable -- deposit immobilization of N according to aluminum by using not less than 650 ** -- a hot-rolling coil -- it can attain covering an overall length mostly. Although the maximum in particular of rolling-up temperature is not defined, when it takes controlling aggravation of descaling nature into consideration, it is good to hold down to below 780 **.

[0026]- With a hot-rolling board, not less than 80% of the amount of N in steel, as AlN, pickling and after cold-rolling is carried out, continuous annealing of the deposit hot-rolling board is carried out. Although a part of dissolution N deposits as AlN in the case of this annealing, since it is a short time, it is difficult to deposit the dissolution N thoroughly. If N of a dissolution state exists after annealing, recovery of the age deterioration in a room temperature, especially breakdown point elongation will become remarkable. For this reason, as for N, it is desirable in the stage of a hot-rolling board not less than 80% or to deposit not less than 85 more% of the amount of N in steel. N of the separation state specified here analyzed AlN by electrolytic extraction analysis usually carried out, and also it puts the amount (N as AlN) ** of N computed from equivalent relations. In order to carry out deposit immobilization of the inside N of steel in a mentioned range, control of the coiling temperature after hot-rolling mentioned above is very important. In addition, they are at least 1-hour or more heat retaining or a means also with leading also cooling slowly about the rolled-round coil.

[0027]- A continuous-annealing continuous annealing process is one of the especially important requirements in this invention. Not less than 3% of hydrogen and the remainder consist of nitrogen substantially, and gas composition carries out continuous annealing held 10 seconds or more to the temperature more than recrystallizing temperature, and makes it produce the decarbonization beyond 0.0005wt% (decarbonizing) in an annealing process in the atmosphere whose dew point is more than -20 **. Thus, by producing decarbonization beyond 0.0005wt% eventually, it becomes possible to reconcile sufficient baking hardenability aimed at by this invention, and the outstanding room temperature-proof prescription nature. Although the detailed mechanism of a decarbonization phenomenon is not necessarily clear, it presumes as follows. Decarbonization uses a surface reaction, and it produces the concentration gradient of big C from a surface toward the inside of a steel plate in a short-time nonequilibrium state in order to remove C in steel from the layer part of a steel plate at a solid breath object reaction as CO (or called CH₃ and CO₂). Although it is difficult to actually analyze the concentration distribution in the board thickness direction of this C, when it calculates by assuming a reaction to be a diffusion limitation of C, it comes to be shown in drawing 1. It can say that this analysis result is appropriate to some extent from corresponding well with C analytical value after [before C content with which it integrated to the board thickness direction annealing] annealing. Such a concentration gradient can maintain this state to a room temperature, if it quenches after soak like continuous annealing (not less than at least 10 **/(sec)).

[0028] Thus, in the attained state of having a concentration gradient of the board thickness direction of C, when secondary rolling of 1 to 5% of rolling reduction is performed, a movable rearrangement will be introduced into the field with very few amounts of C of a layer part. namely, adherence according [the movable rearrangement introduced into a layer part] to C -- easy -- **** -- **** -- it becomes things. By this, the outstanding room temperature-proof prescription nature will appear. On the other hand, in the stage which uses a product, after the plastic-working distortion of not less than about at least 5% is given, aging treatment for about 20 minutes will be performed by about 170 **. In this case, naturally modification is started over the thickness direction whole region of a

steel plate, and many rearrangements are introduced newly. And in the case of prescription, in steel, since the dissolution C of sufficient quantity which adheres these the rearrangements of a lot of remains, the big target baking hardening characteristic is shown.

[0029]In order to produce the above effective decarbonization reactions, it is necessary to consider it as continuous annealing in which rapid heating and forced cooling are possible, and to make the remainder into the annealing atmosphere which consists of nitrogen substantially including not less than 3% of hydrogen in that case, the dew point - more than -20 °C -- desirable -- 1 °C -- it is necessary to consider it as not less than 10 °C, and to perform annealing held 20 seconds or more desirably about 10 seconds or more above recrystallizing temperature Although the maximum in particular of annealing time is not defined, if the efficiency of a actual production process is taken into consideration, it is desirable to use less than 40 seconds. Although the maximum in particular of hydrogen concentration is not defined, if the cost of a controlled atmosphere and the stability of operation are taken into consideration, it is desirable to use 10% or less of concentration. If the amount of C in steel annealing before and after annealing was measured by board thickness direction penetration analysis and the difference has produced the decarbonization which is more than 0.0005wt% as an amount of decarbonization, the outstanding room temperature-proof prescription nature for which it asks, and sufficiently big baking ***** will be obtained. Although the profile of the depth direction should be considered essentially, if it is the steel composition of this invention, and manufacturing conditions, penetration analysis of a board thickness direction can be substituted.

[0030]- Secondary secondary cold rolling cold rolling is usual. Although it carries out at the lightly pressurizing rate of about 0.8%, in order to raise sufficient room temperature-proof prescription characteristic, in this invention, it is necessary to give rolling of rolling reduction higher than these. That is, the breakdown point elongation by prescription in 50 °C 1 three months made into a target can be controlled below to 0.2 % by giving 1% or more of pressing down. However, if pressing down exceeding 5% is performed, the ductility of a steel plate, and since especially uniform elongation falls, the danger of producing faults, such as a crack, at the time of press forming will increase. Therefore, let rolling reduction of secondary cold rolling be the rolling reduction of 1 to 5%. When the room temperature-proof prescription characteristic of having excelled further is required, it is desirable to give a rolling strain with 2 to 3% of rolling reduction.

[0031]the target construction material [this invention] characteristic -- an r value (field Hitoshi Uchihira) -- 1.8 -- the amount of baking hardening (BH) besides above -- more than 40 MPa -- breakdown point elongation after the prescription for 50 °C to three months It may be 0.2% or less. The amount of baking hardening guarantees the strength property at the time of use of forming parts. Although it is changed with the board thickness of a steel plate, and an intensity level, if the value has the amount of baking hardening more than 40 MPa in general in the application parts of the steel plate which has the moldability extremely outstanding like this invention, it is enough in practical use. Although the room temperature prescription characteristics also differ with the target

parts etc., if the prescription for 50 ** 1 three months is borne, it is enough practically in general. If the value of such breakdown point elongation recovered by an aging condition is below 0.2 %, the appearance defect by stretcher-strain generating will not be produced at the time of press forming.

[0032]

[Example]

The example of this invention is described to the primary example. Steel of the component composition shown in Table 1 was ingoted with the converter, hot-rolling, continuous annealing, and secondary cold rolling were performed on the conditions which show this steel slab in Table 2, and the last board thickness was used as the cold rolled sheet steel of 0.7 mm. Thus, from the obtained steel plate, the JIS No. 5 specimen was extracted from one fourth of the positions of the plate width direction, it baked with the usual mechanical property, and hardenability (BH nature) was investigated. About room temperature prescription nature, the thermostat was used for the test piece for tensile test extracted similarly, and prescription for 50 ** 1 three months was given. These results of an investigation are shown in Table 3. Baking hardenability (BH nature) was searched for as follows. That is, after giving 2% of prestrain, unloading was once carried out, the prescription for 20 minutes was given in 170 **, tension was performed again, and the difference of the flow stress in front of prescription and the yield stress after prescription was made into the amount of BHs. The r value was calculated as an average r value with the following formula.

$r = (r_0 + r_{90} + 2r_{45}) / 4$, however r-value r_{45} of a direction that makes an r-value r_{90} :rolling direction and 90 inclination to an r_0 :rolling direction; The r value of a rolling direction and the direction which makes 45 inclination

[0033]

[Table 1]

No	化 学 組 成 (wt%)								備 考
	C	Si	Mn	P	S	Al	N	その他	
1	0.0030	0.01	0.10	0.010	0.004	0.040	0.0015	Nb/0.008	適合鋼
2	0.0022	0.01	0.30	0.005	0.005	0.050	0.0018		適合鋼
3	0.0070	0.01	0.25	0.006	0.001	0.080	0.0025		適合鋼
4	0.0124	0.01	0.15	0.015	0.007	0.028	0.0020	Ti/0.006	適合鋼
5	0.0105	0.01	0.10	0.007	0.008	0.120	0.0022	Mo/0.02	適合鋼
6	0.0012	0.01	0.45	0.006	0.015	0.081	0.0028	Nb/0.006, N/0.0005	適合鋼
7	0.0013	0.01	0.25	0.006	0.009	0.060	0.0011	Cu/0.05, Ni/0.05, Cr/0.05	適合鋼
8	0.0025	0.01	0.55	0.004	0.010	0.050	0.0012	Nb/0.003, Ti/0.005	適合鋼
9	0.0050	0.01	0.15	0.006	0.002	0.040	0.0015		比較鋼

[0034]

[Table 2]

スラブ 加熱温度 (℃)	熱間圧延		熱取り 温度 (℃)	冷間圧延		連続焼鈍				2次冷延 圧下率 (%)
	仕上げ 温度 (℃)	仕上げ 厚み (mm)		厚み (mm)	圧下率 (%)	温度 (℃)	ガス組成	露点 (℃)	時間 (秒)	
1150	880	2.6	750	0.73	72	840	3% H ₂ 残り N ₂	-10	50	2

[0035]

[Table 3]

鋼 No	熱延後の r 値 45 AlH (°)	焼鈍後 C 量 (wt%)	脱炭量 (wt%)	r 値	伸び (%)	TS (MPa)	BH (MPa)	室温時効 後の降伏 伸び (°)	備 考
1	95	0.0009	0.0061	2.1	49	310	45	0	発明例
2	90	0.0011	0.0011	2.0	48	315	47	0	発明例
3	95	0.0005	0.0005	1.8	46	330	51	0	発明例
4	85	0.0040	0.0044	1.8	45	340	50	0	発明例
5	85	0.0080	0.0025	1.8	45	350	52	0	発明例
6	95	0.0006	0.0006	2.0	49	309	41	0	発明例
7	95	0.0004	0.0009	1.9	46	380	55	0	発明例
8	90	0.0015	0.0010	1.9	47	330	48	0	発明例
9	82	0.0020	0.0030	1.1	43	350	50	7.0	比較例

[0036]The steel plate manufactured by this invention method being extended with a high r value, having (EI), and having the baking hardening characteristic more than 40 MPa from Tables 1-3, by severe prescription, since breakdown point elongation is not produced, the appearance defect what is called accompanying stretcher-strain generating is not produced, either. Also in press forming with this actual, the rise of the part intensity by BH nature as expected and control of stretcher-strain generating were attained. Although experimented by setting annealing conditions as the range of this invention like the above experiment with the continuation hot-dip-zinc-coated-carbon-steel-sheet production line, the outstanding moldability (a high r value, high EI) and high BH nature were obtained like the case of the cold rolled sheet steel mentioned above, and there was no degradation by room temperature prescription. Therefore, it turned out that this invention is satisfactorily applicable also not only to cold rolled sheet steel but a hot-dip zinc-coated carbon steel sheet (and alloying hot-dip zinc-coated carbon steel sheet). Although it is natural, it is [after manufacturing cold rolled sheet steel] satisfactorily [at all] applicable also to the use which performs electrogalvanizing etc.

[0037]Cold rolled sheet steel was manufactured to the steel 1 of the example 2 table 1 by the manufacturing conditions shown in Table 4, and the Zn-nickel alloy-plating steel plate was manufactured in the continuous system electroplating line. Then, after painting and burning resin on the surface, mechanical properties, BH nature, and the age deterioration characteristic in the room temperature were investigated like Example 1. The result is shown in Table 5. Since the resin coating composite-coatings steel plate

manufactured by this invention method does not produce breakdown point elongation in the above severe prescription, having a high r value and elongation and having the baking hardening characteristic of 40 or more MPa, it does not produce the appearance defect accompanying stretcher-strain generating. Also in actual press forming, the rise of the part intensity by BH nature as expected and control of stretcher-strain generating were attained.

[0038]

[Table 4]

No	スラブ加熱温度 (°C)	熱延仕上げ温度 (°C)	巻取り温度 (°C)	熱延後のN中N 68 A1N (%)	冷延圧下率 (%)	連続焼鈍				炭炭量 (wt%)	2 次冷延圧下率 (%)	備 考
						温度 (°C)	ガス組成	露点 (°C)	時間 (秒)			
1	1150	880	680	90	75	850	50H ₂ - 残N ₂	-10	25	21	2	発明例
2	1160	900	710	95	75	880	40H ₂ - 残N ₂	-15	30	18	3	発明例
3	1150	910	550	85	80	840	40H ₂ - 残N ₂	-5	20	22	3	発明例
4	1100	850	700	90	73	840	50H ₂ - 残N ₂	0	15	25	2	発明例
5	1120	850	710	90	73	840	50H ₂ - 残N ₂	-10	20	22	1.5	発明例
6	1250	900	680	85	78	830	50H ₂ - 残N ₂	-15	35	20	2	発明例
7	1230	900	680	85	78	830	50H ₂ - 残N ₂	-15	20	20	2	発明例
8	1200	900	690	85	75	820	40H ₂ - 残N ₂	-10	15	23	2	発明例
9	1200	870	700	96	75	840	40H ₂ - 残N ₂	-10	20	22	1.5	発明例
10	1200	900	540	70	75	820	40H ₂ - 残N ₂	-10	20	20	1.5	比較例
11	1200	880	710	82	75	840	N ₂ ~100 %	-10	20	1	1.5	比較例
12	1200	830	700	83	75	840	40H ₂ - 残N ₂	-10	20	22	5	比較例

[0039]

[Table 5]

No	r 値	伸 び (%)	TS (MPa)	BF (MPa)	室温時効 後の降伏 伸び (%)	摘 要
1	2.02	48	315	45	0	発明例
2	2.14	49	310	42	0	発明例
3	1.95	47	320	43	0	発明例
4	2.05	49	315	41	0	発明例
5	1.98	48	325	43	0	発明例
6	2.10	49	312	44	0	発明例
7	1.85	47	330	45	0	発明例
8	1.88	47	331	51	0	発明例
9	1.92	46	325	44	0	発明例
10	1.40	46	320	45	0.5	比較例
11	1.70	45	325	45	1.5	比較例
12	1.78	33	380	20	0	比較例

[0040]

[Effect of the Invention] In [according to / as explained above / this invention] the continuous annealing process hot-rolling and after carrying out cold-rolling the steel stock of the specific component range, It becomes possible by being decarbonized, forming the concentration distribution of C in a board thickness direction positively, and giving temper rolling higher further comparatively to both be stabilized and to satisfy the difficult, sufficiently big paint baking hardenability and the outstanding age deterioration-proof characteristic of making it conventionally compatible. Therefore, since the steel plate by this invention shows the part intensity which rose and excelled [hardening / baking] in intensity greatly when it is excellent in a moldability and is actually used as a product by elasticity at the time of press forming and an assembly, the gauge down of a steel plate required to obtain same part intensity of it is attained. Although it is natural, the steel plate by this invention can be used also as various kinds of plating negatives.

